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(54) Name of the Invention: A METHOD TO MANUFACTURE ULTRA-HIGH
MOLECULAR POLYMER HAVING MONODISPERSE CHARACTERISTICS

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SPECIFICATIONS

1. Title of the Invention: A Method To Manufacture Ultra-High Molecular Polymer Having Monodisperse Characteristics

2. Scope of the Patent's Claims:

1. A method to manufacture ultra-high molecular polymer having monodisperse characteristics show molecular weight is at least 5,000,000,

characterized by the fact that it comprises an emulsion polymerization method using at least one type of a monomer containing a vinyl group having the radical polymerization function, comprising a redox-based polymerization initiator using 0.001 ~ 0.2 parts by weight of a hydroperoxide or persulfate and 3 ~ 50 parts by weight of an emulsifier per 100 parts by weight of at least one type of said monomer.

2. The method to manufacture ultra high-molecular polymer having monodisperse characteristics described in claim 1, characterized by the fact that the redox-based polymerization initiator is hydroperoxide-ferrous phosphate glucose-sodium pyrophosphate, hydroperoxide-hydroperoxide-ferrous sulfate-dextrose-sodium pyrophosphate-sodium phosphate, hydroperoxide-ferrous sulfate-sodium pyrophosphate-sodium phosphate, hydroperoxide-ferrous phosphate-formaldehyde sodium sulfoxylate ethylene diamine acetate, persulfate-hexacyano metal (II)-sodium and persulfate-sodium thiosulfate-copper sulfate.

3. Detailed Description of the Invention:

This invention relates to a method to manufacture an ultra-high polymer having monodisperse characteristics with the emulsion polymerization method under specific conditions.

It is known from prior art that polystyrene, polymethyl methacrylate, polybutadiene, etc., can be manufactured with the emulsion polymerization method. However, the polymers which were obtained according to these conventional methods were not only characterized by a narrow distribution of the molecular weight of the polymer, but it was also difficult to obtain polymers with a molecular weight above 5,000,000. On the other hand, the living anion polymerization method is also known as a method which can be used to obtain polymers in the monodisperse status with a narrow distribution of molecular weight, and monodisperse polystyrene, polyethylene oxide, etc., manufactured according to this polymerization method is presumably commercially available.

However, because this living anion polymer method requires a highly pure monomer material, it is also necessary to perform dehydration, etc., during polymerization, and the polymerization initiator becomes inactivated if even a trace amount of impurity is present. Moreover, because a highly sophisticated polymerization technique is required, this method is not suitable for industrial manufacturing.

Incidentally, it has been reported recently that emulsion polymerization was conducted which resulted in living polymerization conduct characteristics with a polyamine activator when polypropylene acetate was used as an initiator with ozone oxidation in isotactic polypropylene. However, because polypropylene peroxide is used according to this method as the initiator, the problem is that the separation of the initiator from the polymer obtained in this manner is complicated requiring a method for ozone oxidation in propylene, and also methods for handling of oxides are complicated, which means that these methods are again not suitable for industrial manufacturing.

Another method proposed was an attempt to use dialkyl peroxide as an initiator and first class amine alkyl or second class amine as the activator in an initiator system to perform emulsion polymerization as a method to manufacture ultra-high molecular polymer having monodisperse characteristics. However, when this method is used, the characteristics of the polymerization initiator are poor and the polymer has a turbid color which is thought to be due to amines. Another phenomenon displayed is that reaction is not completed during polymerization so that the polymerization reaction must be in the end stopped if large amounts of trace residues or unreacted monomers are left due to the polymerization inhibitor. This means again that this method is again not suitable for industrial manufacturing.

In view of the above described problems, the inventors of this invention attained the purpose of this invention after an intensive research of methods enabling to manufacture in a stable way ultra-high molecular polymer having monodisperse characteristics with an optimal initiating agent by discovering an ultra high-molecular polymers having monodisperse characteristics which can be manufactured in a relatively short period of time by applying control using a very large micellar weight and a high polymerization speed achieved with an emulsifier in the entire polymer system, wherein the amount of the generated radicals is controlled by the amount of added initiator, using a redox type of a polymerization initiating agent as a specific required component of a specific compound.

Specifically, the gist of the present invention can be described as follows. The invention relates to a method to manufacture an ultra-high molecular polymer having monodisperse characteristics whose molecular weight is at least 5,000,000, characterized by the fact that 3 ~ 50 parts by weight of an emulsifier is used together with 0.001 ~ 0.2 parts by weight of persulfate or hydroperoxide in the composition of a redox type of an initiating agent per at least 100 parts by weight of at least one type of monomer with at least one type of an emulsion polymerization method utilizing at least a monomer containing a vinyl base having the radical polymerization function.

The structural components of hydroperoxide according to conventional methods which used the redox type of an initiator with the emulsion polymerization method were based on a wide distribution of molecular weight using a high ratio between the mean molecular weight M_w of the obtained monomer and the mean numerical molecular weight M_n (M_w/M_n). In addition, under these conditions it was possible only to obtain a molecular weight in the range of several hundred thousand to about one million. Also, when such redox types of polymerization initiators are used, no means is provided which would make it possible to control the amount of the generated radicals and that this why this will result in a wide distribution of the molecular weight of the polymer produced in this manner.

In contrast to these conventional methods, according to the emulsion polymerization method used by this invention, a redox type of a polymer initiator is used with hydroperoxide or persulfate as an indispensable component, and because only a very small trace amount of this initiator is used, this makes it possible to control the amount of generated radicals. In addition, this method is also completely different from conventional concepts of emulsion polymerization methods because its major characteristic is that the amount of the emulsifier is increased when the polymerization speed is reduced based on the used trace amount of the initiator.

According to an embodiment of the present invention it is possible to use as a monomer which contains a vinyl group having the radical polymerization function for instance styrene, α -methyl styrene, methyl styrene or a similar aromatic alkenyl compound; methyl methacrylate, ethyl methacrylate, butyl methacrylate or a similar methacrylic ester; methyl acrylate, ethyl acrylate, butyl acrylate or a similar acrylic ester; acrylonitrile; methacrylonitrile, ethylene,

propylene; butadiene, isoprene, chloroprene or a similar diolefin conjugate; vinyl acetate; vinyl chloride; vinylidene chloride; aryl methacrylate; triaryl isocyanurate; ethylene diamethacrylate, or a similar content can be used, either singly or as a mixture.

For the redox-based polymerization initiator according to this invention it is possible to use an initiator having hydroperoxide or persulfate as an indispensable component and the amount of hydroperoxide or persulfate that should be used is in the range of 0.001 ~ 0.2 parts by weight per 100 parts by weight of at least one type of a monomer containing a vinyl group having said radical polymer function, although the range of 0.01 ~ 0.1 parts by weight is optimal.

If the amount used is less than 0.001 parts by weight, polymerization will not be completed. On the other hand, if this amount exceeds 0.2 parts by weight, the polymerization degree of the polymer will be reduced, which is not desirable either. Among concrete examples of said redox type of polymerization initiators are hydroperoxide-ferrous sulfate-glucose-sodium pyrophosphate, hydroperoxide-ferrous sulfate-dextrose-sodium pyrophosphate-sodium phosphate, hydroperoxide-ferrous sulfate-sodium pyrophosphate-sodium phosphate, hydroperoxide-ferrous phosphate-formaldehyde sodium sulfoxylate ethylene diamine acetate, persulfate-hexacyano metal (II)-sodium and persulfate-sodium thiosulfate-copper sulfate, and also other examples can be named. In addition, for hydroperoxide it is possible to use cumene

hydroperoxide, t-butyl hydroperoxide, diisopropyl benzene hydroperoxide, P-methane hydroperoxide, 1,1,3,3-tetramethyl butyl hydroperoxide, 2,5-dimethyl hexane-2,5-dihydroperoxide and other items can be used. In addition, for persulfate it is possible to use potassium persulfate or ammonium persulfate, etc.

The reducing agent which can be used for said redox-based polymerization initiator in the embodiment of this invention is glucose, dextrose, formaldehyde sodium sulfoxylate, sodium thio persulfate, or a similar activating agent can be used with ferrous sulfate, sodium pyrophosphate, sodium phosphate, potassium hexadimino metal (II), ethylene diamino acetate, copper sulfate, or a similar component can be used.

It is also possible to use an anionic or non-ion emulsifier for the emulsifier of this invention, and the amount of the emulsifier that should be used should correspond to 3 ~ 50 parts by weight per 100 parts by weight of at least one type of said monomer having a vinyl group, although the range of 5 ~ 30 parts by weight is optimal. If the amount of the used emulsifier is less than 3 parts by weight, the speed of polymerization will be slow and at the same time, the molecular weight of the polymer weight will be low, which is not desirable. On the other hand, even if more than 50 parts by weight is used, this will not result in any changes of the speed of polymerization or of molecular weight, which means that it is unnecessary.

The following is a detailed explanation of an embodiment mode of this invention.

First, emulsion polymerization is performed under customary emulsion polymerization conditions by applying a temperature in the range of -20°C ~ 70°C to the compound comprising the emulsifier, redox-based polymer initiator and the specified monomer. It is desirable if the polymerization temperature is in the range of 20°C ~ 50°C because this makes it possible to obtain optimal results of emulsion polymerization.

The water which is used during this polymerization can be ion-exchange water which is commonly used for emulsion polymerization or it is also possible to use pure water. The amount of water that should be used is identical to normal emulsion polymerization conditions, that is to say 100 ~ 1,000 parts by weight per 100 parts by weight of the monomer, although the range of 150 ~ 500 parts by weight is optimal. In addition, when emulsion polymerization is conducted, a chain transfer agent or a molecular weight adjusting agent is not used unless there is a particular reason for that in order to broaden the distribution of molecular weight. After the polymerization is finished, the product can be used as is as latex.

According to the method of this invention, the above mentioned polymer ratio between Mw and Mn (Mw/Mn) should be no more than about 1.5. This is a sufficiently narrow molecular weight ratio distribution of a polymer displaying monodisperse characteristics. Moreover, when an ultra high-molecular polymer with a molecular weight of at least 5,000,000 is used, such a polymer can be manufactured with a common emulsion polymerization method enabling conditions which are close to industrial manufacturing conditions, which has a great merit for the

purposes of industrial manufacturing.

According to the method of this invention, the polymer emulsion can be manufactured with a very high solution viscosity even if a low concentration is used,

It is also possible to form a film from the polymer emulsion. Graft-polymerization can be also induced if the polymer is mixed with another high-molecular material which can be used to improve the mechanical capacity of the high-molecular material and various other characteristics can be achieved depending on the use for which the polymer is obtained.

The following is an explanation of a concrete embodiment of the present invention. In addition, since the polymer obtained according to the method of this invention should be an ultra high-molecular polymer, a confirmation of the narrow range of the distribution of its molecular weight was performed based on a monodisperse polystyrene standard sample (molecular weight 6,200,000, $M_w/M_n = 1.14$) manufactured by Toyo Totatsu K.K. Company, using a comparison of the gel permeation chromatography (GPC) and the resulting curve was displayed (with an index of refraction detector and a low angle optical diffusion detector) indicating specific viscosity (η). The GPC measurement was performed at room temperature in tetrahydrofuran solvent. In addition, the (η) value was determined from the solution viscosity by measurements conducted at 25°C in chloroform solvent.

Embodiment 1

After 160 g of styrene, 800 g of a 5 weight % aqueous solution of dodecyl benzene sodium sulfonic acid was added together with the various amounts of redox-based polymerization initiators shown in Table 1 to a three-way flask equipped with a stirring device, thermometer and condenser, polymerization was conducted for 5 hours in nitrogen air current at 40°C, 2 ml of an aqueous solution of hydroquinone with a concentration of 1 mol/l was added, the polymerization was stopped and 6 polymer redox types were obtained. The different polymer redox types were then dripped into isopropanol and polymer sedimentation was induced. This was followed by washing in water, drying under reduced pressure, and a measurement of the yield of these polymers, of the (η) value and GPC measurements. The molecular weight of polystyrene and the M_w/M_n ratio were then calculated and determined on the basis of the results of the GPC measurements. These results are shown in Table 1. As shown in Table 1, the amount of the added redox-based polymerization agent (styrene) was calculated as 160 g per 100 parts by weight of the polymer (the same ratio will be also used hereinafter unless specified otherwise).

In addition, Figure 1 shows one example of a GPC measurement curve. As shown in the same figure, curve A indicates the polymer from test number 2, while dotted curve B indicates said monodisperse polystyrene standard sample. It is clear from Figure 1 that the polymer of this invention displays not only monodisperse characteristics, but also that it is an ultra high-molecular polymer.

Table 1

Sample #	Redox-Based Polymer Initiator						Yield	Specific Viscosity	Molecular Weight Calculated from Polystyrene Conversion	Mw/Mn
	Hydroperoxide or Persulfate	Parts by Weight	Reducing Agent	Parts by Weight	Activating Agent	Parts by Weight				
1	cumene hydroperoxide	0.1	glucose	0.5	sodium pyrophosphate	0.5	90	10.3	600	1.34
					ferrous sulfate	0.01				
					sodium pyrophosphate	0.1				
2	cumene hydroperoxide	0.1	dextrose	0.15	sodium phosphate	0.02	93	11.6	720	1.30
					ferrous sulfate	0.003				
3	cumene hydroperoxide	0.02			sodium pyrophosphate	0.1	85	9.0	520	1.46
					sodium phosphate	0.002				
					ferrous sulfate	0.01				
4	potassium persulfate	0.2			hexacyano metal (II) potassium	0.05	85	86	500	1.48
5	potassium persulfate	0.03	sodium thiosulfate	0.01	copper sulfate	0.0002	98	15.5	1100	1.15
6	t-butyl hydroperoxide	0.05	formaldehyde sodium sulphonylate dihydrate	0.1	ethylene diamine acetate	0.005	98	14.8	1000	1.20
					ferrous sulfate	0.001				

Embodiment 2

0.1 parts by weight of the respective peroxides shown in Table 2 was used instead of 0.1 parts by weight of cumene hydroperoxide from sample number 2 in Embodiment 1. The

conditions for polymerization were otherwise identical. In addition, sedimentation, washing with water, and drying under reduced pressure was conducted again and the results were evaluated according to the same method as in Embodiment 1. The results are shown in Table 2.

As one can see from the results shown in Table 2, hydroperoxide resulted in manufacturing of an ultra-high molecular weight monodisperse polystyrene, and polymerization did not take place with dialkyl peroxide and ester.

Table 2

Sample #	Peroxide	Yield (%)	Specific Viscosity (η)	Molecular Weight Calculated from Polystyrene Conversion	Mw/Mn
1	7-butyl hydroperoxide	98	14.5	1000	1.24
2	diisopropyl benzene hydroperoxide	96	11.2	680	1.20
3	P-methane hydroperoxide	96	12.0	720	1.44
4	1,1,3,3-tetramethyl butyl hydroperoxide	90	9.5	610	1.50
5	2,5-dimethyl hexane -2,5-dihydro peroxide	92	0.4	560	1.42
6	t-butyl cumyl peroxide	0	-	-	-
7	2,5-dimethyl-2,5-di-t-butyl peroxyhexene	0	-	-	-
8	t-butyl peroxyacetate	0	-	-	-

Embodiment 3

Except for the fact that the various types of monomers which are shown in Table 3 were used instead of 160 g of styrene from sample number 2 of Embodiment 1, the polymerization conditions were identical. In addition, sedimentation, washing with water, and drying under reduced pressure was conducted again and the results were evaluated according to the same method as in Embodiment 1. The results are shown in Table 3.

Table 3

Sample #	Peroxide	Amount of Used Monomer (g)	Yield (%)	Specific Viscosity (η)	Molecular Weight Calculated from Polystyrene Conversion $\times 10^{-4}$	Mw/Mn
1	α -methyl styrene	160	90	10.5	1200	1.33
2	methyl methacrylate	160	99	25.5	1400	1.15
3	butyl acrylate	160	99	12.0	2100	1.21
4	acrylonitrile	160	95	8.5	840	1.45
5	butadiene	160	98	-	-	-
6	vinyl acetate	160	98	13.0	500	1.42
7	vinyl chloride	160	96	27.6	670	1.22
8	butyl acrylate aryl methacrylate styrene	158.4 1.6 80	98	-	-	-
9	methyl methacrylate	80	99	15.5	1100	-

Embodiment 4

Using the same conditions as those of Embodiment 1, 0.05 parts by weight of t-butyl hydroperoxide, 0.1 parts by weight of formaldehyde sodium sulfoxylate dihydrate, 0.005 parts by weight of ethylene diamino acetate, and 0.001 parts by weight of ferrous sulfate were added to the monomer as a redox-based polymerization agent. Next, 100 g of butyl acrylate was added and polymerization was conducted for 5 hours.

In addition, after 100 g of styrene was added, polymerization was continued for another 5 hours. In this case, the weight ratio of said redox-based polymer initiator is indicated as 100 parts by weight when the total amount of butyl acrylate, styrene, and methyl methacrylate was 300 g.

The polymer was then separated from the latex which was obtained in this manner with the same operations which were used also in Embodiment 1. These operations were then followed by washing with water, drying under reduced pressure, and the evaluation of polymerization was

performed before styrene was added, before methacrylate was added, and again after methacrylate was added. The results are shown in Table 4. As shown by the GPC curve indicated in Figure 2, curve C indicates butyl acrylate polymer before styrene was added, and curve D indicates the polymer after styrene was added. The figure indicates that molecular weight shifted to the high-molecular weight side with block copolymerization.

As one can see from a comparison of physical characteristics, it is clear that the polymer which was ultimately obtained was a block copolymer.

Figure 4

	Yield	Specific Viscosity (η)	Molecular Weight Calculated from Polystyrene Conversion	Mw/Mn
after polymerization of butyl acrylate	95	10.5	1900	1.16
polymerization after styrene was added	195	27.6	2200	1.21
polymerization after methyl acrylate was added	287	25.5	2900	1.30

Comparative Example

Using the same three-way flask which was used in Embodiment 1, 160 g of styrene was added to 800 g of 1 weight % aqueous solution of dodecyl benzene sodium sulfonate and the respective amounts of redox-based polymerization initiators which are shown in Table 5 were fed into the flask. Three types of polymers were obtained when the same operation as those indicated in Embodiment 1 were performed. The only exception was that the polymerization was conducted for 5 hours in nitrogen air current at 70°C. These polymers were then evaluated according to the same conditions which are indicated in Embodiment 1. The results are shown in Table 5.

As one can see from the results indicated in Table 5, it is clear that the degree of polymerization of these polymers was small, and since the Mw/Mn value was high, their molecular weight was distributed in a wide range.

Table 5

Sample #	Redox-Based Polymerization Initiator					Parts by Weight	Yield (%)	Specific Viscosity (η)	Calculated Molecul. Weight $\times 10^{-4}$	Mw/Mn
	hydroperoxide or persulfate	parts by weight	reducing agent	parts by weight	activator					
1	cumene hydroperoxide	0.5	glucose	1.0	sodium pyrophosphate	1.0	98	4.5	200	2.10
					ferrous sulfate	0.1				
2	t-butyl hydroperoxide	0.3	formaldehyde sodium sulfoxylate dihydride	0.5	ethylene diamino acetate	0.01	99	5.1	240	2.03
					ferrous sulfate	0.005				
3	potassium persulfate	0.3	thio-sulfate sodium	0.5	copper sulfate	0.01	98	3.8	160	1.96

4. Simple Explanation of Figures

Figure 1 and Figure 2 show GPC curves of a polymer. Curve A shown in Figure 1 represents sample number 2 of Embodiment 1, while curve B indicates a monodisperse polystyrene standard sample. In addition, curve C shown in Figure 2 represents a butyl acrylate polymer of Embodiment 4 before styrene was added, while curve D indicates a GPC curve after the styrene addition and polymerization.

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[Figure 1]

- 1 index of refraction detector
- 2 low angle optical diffusion detector
- 3 GPC count

[Figure 2]

- 1 index of refraction detector
- 2 low angle optical diffusion detector
- 3 GPC count

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図 1

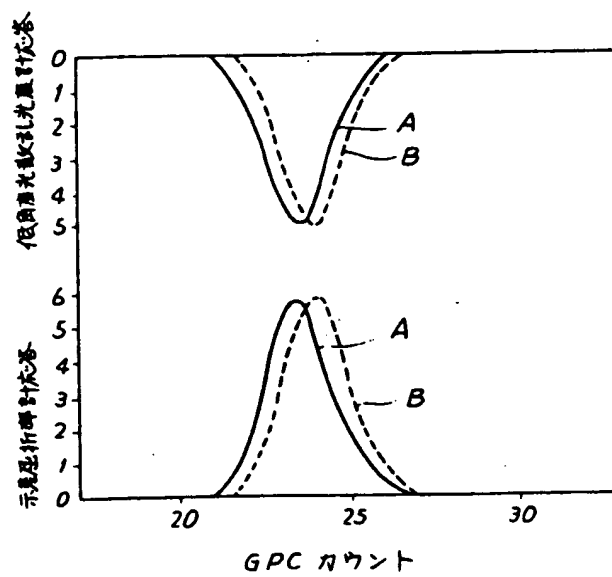


図 2

